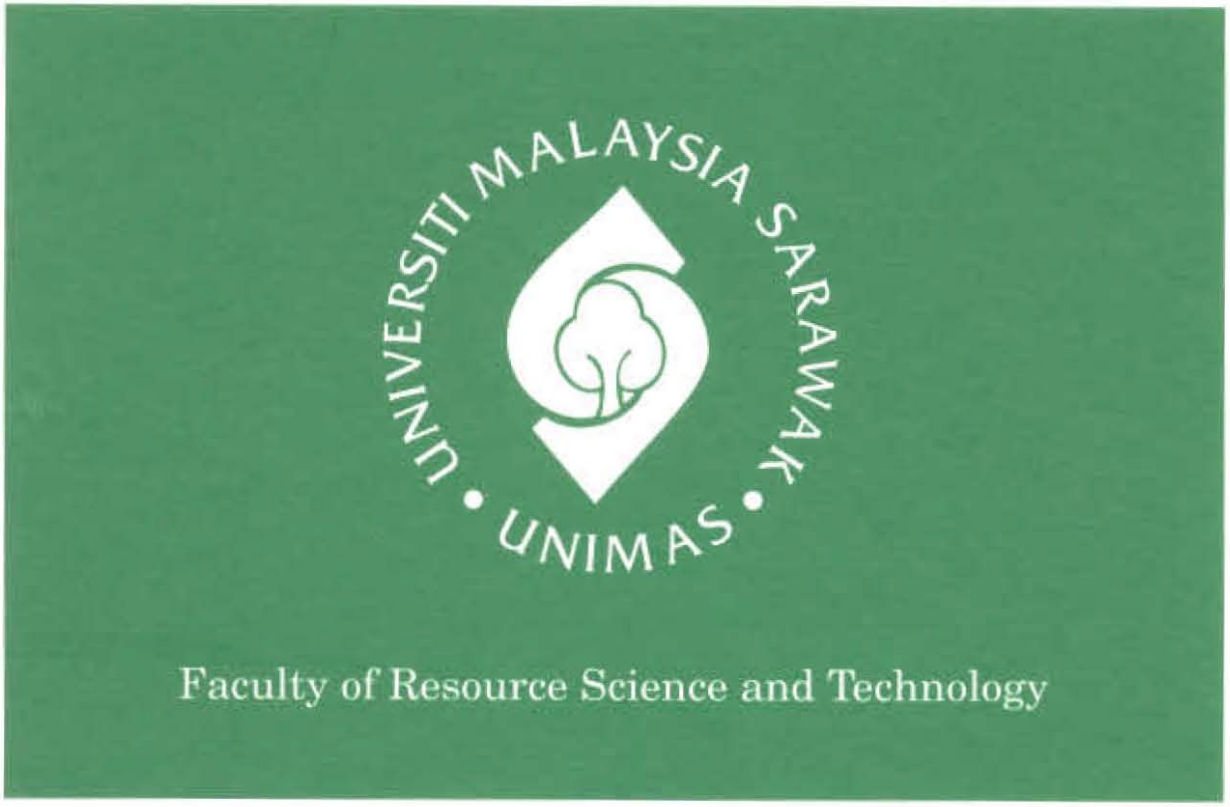

EFFECTS OF NITROHUMIC ACIDS ON THE AGGREGATE STABILITY OF LOAMY SAND

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Bachelor of Science with Honours
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DECLARATION

No portion of the work referred to in this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.

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TABLE OF CONTENTS

Effects of Nitrohumic Acids on the Aggregate Stability of Loamy Sand

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ABSTRACT

In this research, effects of nitrohumic acids derived from Mukah coal on aggregate stability of loamy sand obtained from Batu Tujuh were determined. 6 rates of nitrohumic acids (0.0, 0.05, 0.10, 0.50, 1.0, 10 g/kg) were applied to the soil at the incubation period of 15 days. 5 sequences of wetting and drying cycles (1, 2, 3, 4, 5 cycles) were carried out using 2-1 mm aggregates of treated soils and then evaluated for any improvement in aggregate stability. Compared with the control, the treated soils showed significant improvement in aggregate stability and also reduced substantially the disaggregating effects of wetting and drying cycle. Low rate of nitrohumic acids (0.10 g/kg) gave improvement but higher rates were ineffective and reduced the aggregate stability of the soils. However, the rate of 10.0 g/kg also showed some potential effect to the aggregate stability.

Keywords: Aggregate stability, wetting and drying cycles, Nitrohumic acids, loamy sand.

ABSTRAK

Dalam kajian ini, kesan asid nitrohumik ekstrak dari arang batu Mukah ke atas kestabilan aggregat tanah loam berpasir dari Batu Tujuh telah ditentukan. Enam kadar asid nitrohumik (0.0, 0.05, 0.10, 0.50, 1.0, 10 g/kg) telah diaplikasikan ke atas sampel tanah dan diinkubasi selama 15 hari. 5 siri kitar pengeringan dan pembasahan (Kitar 1, 2, 3, 4, 5) telah dijalankan menggunakan aggregat 2-1 mm dan kemudian dinilai peningkatan kestabilan aggregatnya. Berbanding dengan kawalan, tanah yang diaplikasikan dengan asid nitrohumik menunjukkan peningkatan secara signifikan dalam kestabilan agregatnya dan juga telah mengurangkan nyah-gumpal kesan daripada kitar pengeringan dan pembasahan. Kadar rendah asid nirohumik (0.10g/kg) memberikan peningkatan tetapi kadar yang lebih tinggi adalah tidak efektif dan menurunkan kestabilan aggregat tanah. Walau bagaimanapun, kadar 10.0g/kg juga menunjukkan potensi ke atas kestabilan aggregat.

Kata kunci: Kestabilan agregat, kitar pengeringan dan pembasahan, asid nitrohumik, loam pasir.

1. INTRODUCTION

Humic substances are dark-colored organic substances with high molecular weight (2000 to 300,000 g/mol) that make up 60 to 80% of soil organic matter (Brady and Weil, 2002). They are commonly found in peat water, soil, coal and other natural materials (Novák *et al.*, 2001). Humic substances can be separated into three fractions: humic acids, fulvic acids and humins (Hayes and Wilson, 1997). A fraction of humic substances that are insoluble in water under acidic condition but becoming soluble in basic condition are known as humic acids (Faithfull, 2002).

Humic acids are used as a soil conditioner in agriculture applications. They are vital for maintaining the crumb structure of soils, sustaining the water regime, holding micronutrients and acting as an acid-base buffer in soils (MacCarthy, 1989). Small quantities of humic acids (in the range of 50-300 mg/L) were found to enhance the growth of plant shoots and roots significantly (Brady and Weil, 2002).

Humic acids were also reported to improve the aggregate stability of soils (Brady and Weil, 2002). Addition of humic substances extracted from an oxidized coal to soil was revealed to retard the onset of runoff process under rainfall (Piccolo and Celano, 1994). In another study, a reduction in erosion rates was similarly observed in soils amended with humic acids suggesting the potential of humic acids as soil conditioner in improving aggregate stability (Piccolo *et al.*, 1997). Numerous humate products such as potassium humate and potassium fulvate have been commercialized to improve the soil aggregate stability and they are well accepted by the agriculture community (Imbufe *et al.*, 2005). Application of humic acids,

particularly coal derived humic acids, appears to be a potentially effective soil management practice for reducing soil erosion rates. Nevertheless, the potential of the indigenous coal derived humic acids on the aggregate stability of soils is scarcely known.

The objective of this study is to investigate the potential of the indigenous Mukah coal derived humic acids, with particular interest on the nitrohumic acids, in improving the aggregate stability of loamy sand soils.

2. LITERATURE REVIEW

2.1 Basic characteristics of humic acids

Aiken *et al.* (1985) defined humic substances as "*a general category of naturally occurring heterogeneous organic substances that can generally be characterized as being yellow to black in colour, of high molecular weight, and refractory*". It is among the most widely distributed organic matter; commonly found in soils, natural water, sewage, coals and miscellaneous deposits (Stevenson and Cole, 1999).

Humic substances are a mixture of large complex molecules (molar masses 20,000- 100,000 g mol^{-1}) and mainly consisting of humic and fulvic acids, which are produced from nitrogenous compounds containing decomposed amino acids and aromatic complexes. Humic acids are the alkali soluble fraction of humic substances that can affect the physical and chemical properties of soils due to its carboxyl (-COOH) and phenolic (-OH) groups (Faithfull, 2002; Kütük *et al.*, 1965). According to Tan (1994), humic acids enhance the soil structure formation; increase the soil water-holding capacity and the cation exchange capacity.

Application of low rates of humic acids has been well reported to improve the soil aggregate stability. According to Piccolo *et al.* (1997) erosion susceptible soils amended with low rates of coal derived humic substances evidenced a reduction in the erosion rates. The mechanism by which humic acids induces greater stability on soil aggregates is explained by the formation of clay-humic complexes through bridging polyvalent cations adsorbed on clay surfaces (Piccolo and Mbagwu, 1994). This orients the chelating acidic functional groups of

humic materials towards the interior of the aggregates, leaving the aliphatic and aromatic hydrophobic components facing outwards from the soil particle to form a water repellent coating that reduces water infiltration into the aggregates.

The amount of extracted humic acids from coal can be increased by oxidizing the sample via regeneration process (Piccolo *et al.*, 1997). Regeneration process can be achieved by using oxidizing agent such as nitric acid (HNO_3) and the humic acids prepared with this process are referred to as nitrohumic acids (NHAs). The nitrohumic acids may differ from the humic acids and comprise additional nitrogen content.

2.2 Properties of loamy sand (an erosion susceptible soil)

Loamy sand is an intermediate in texture and properties between fine (contains a large proportion of clay) and coarse (contains a large proportion of sand) textured soil (Brady, 1990; http://en.wikipedia.org/wiki/Soil_texture). This soil is dominated by sand, which comprises at least 70% of the soil by weight with less than 20% of clay fraction (Brady and Weil, 1996; Dutarte *et al.*, 1993). The high fraction of sand and low fraction of clay can affect the stability and fertility of the soil. Evans (1980) revealed that soils with a clay fraction between 9 to 30% are the most suseeptible to erosion and possessing poor nutrient holding capacity. Commonly, loamy sand has high bulk density with variation of 1.20-1.80 Mg/m^3 (Brady, 1990). Besides, it is also contains low organic matter (<2%) which partly explains its weak structure and low stability to rainfall and erosion (Dutartre *et al.*, 1993). The weak structure of the soil leads to less aggregation and low water holding (Brady, 1990).

2.3 Aggregate stability

Aggregate stability refers to the ability of soil aggregate to resist disruption when external forces are applied. It is important to maintain the soil porosity and increase the stability against wind and water erosion (Magdoff and Weil, 2004). Aggregate stability is affected by soil texture and type of organic matter present that helps to hold the aggregate together (soils.usda.gov/sqi/files/sq_eig_1.pdf). In a study on the influence of the organic materials on the aggregate stability of soils from Lamporecchio, Cremona and Vicarello (in Italy); results revealed an improved stability for Lamporecchio and Cremona soils (at 10% and 6%, respectively) but a decrease in Vicarello soils. This was related to the texture of soil suggesting that the soils from Lamporecchio, Cremona and Vicarello were sandy laom, sandy clay loam and clay, respectively (Mbagwu, 2003). Conclusion was drawn that stable soils benefit more from the application of organic materials than the less stable soils.

Deterioration in soil aggregate stability is attributed to a decline in soil organic matter which results in reduced infiltration rates, increased slaking and crusting, and accelerated runoff erosion and poor crop productivity (Mbagwu, 2003; Piccolo *et al.*, 1997). In agricultural soils, the organic matter and other organic compounds (from bacteria and fungi) are the major binding agent responsible for aggregate stability. According to Plaster (1992), the organic carbon in humus aids aggregation. This causes the soil particles to bind together to form soil aggregates. More importantly, the gummy substances produced by soil organisms during the decay of organic matter also bind the soil clump resulting in a stable soil condition (illustrated in Figure 1).

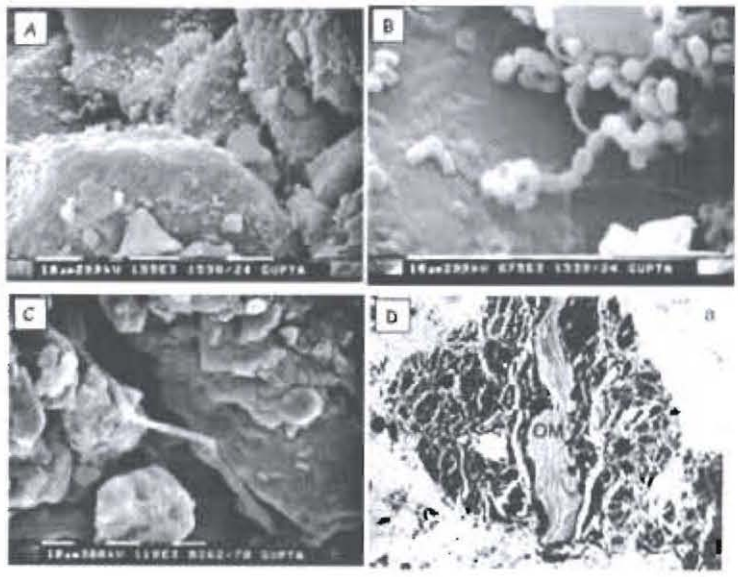

Figure 1: Location of bacteria (A and B), fungi (C) and organic matter (D) within soil matrix (adapted from www.grdc.com.au)

Imbufe *et al.* (2005) in addition revealed that the soil stabilization occurred as a result of the formation of clay-humate complexes, which protect the soil from disaggregating effects. Therefore, soil under intensive agriculture will require an organic amendment to improve its aggregate stability by increasing soil organic matter.

3. MATERIALS AND METHOD

3.1 Soil analyses

Soil samples were collected at 0-20 cm depth from the Tentera Udara Di-Raja Malaysia (TUDM) construction site at Batu Tujuh and air dried at room temperature. The bulk samples were classified according to the soil texture triangle developed by the US Department of Agriculture. Figure 2 illustrates the soil triangle classification.

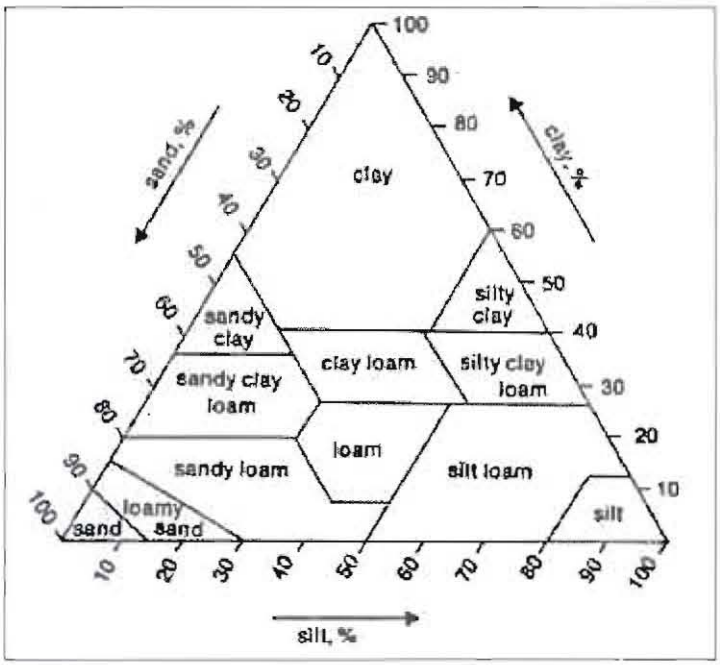

Figure 2: Soil triangle classification

The fresh soil samples were subjected to particle size analysis, moisture, organic matter and pH analyses.

3.1.1 Particle size analysis (Pipette Method)

Ten grams of 2 mm soil was added to 20 ml of H_2O_2 and left overnight. The mixture was boiled with 5 ml of sodium hexametaphosphate and transferred to a 600 ml beaker. The volume was made up to 500 ml with distilled water, stirred for 10 minutes and transferred to a 1 L cylinder. The volume was then made up to 1L with distilled water. Twenty mililiters of suspension was withdrawn from a depth of 10 cm below the surface and this fraction is referred to as silt and clay. Clay fractions were obtained from a depth of 6 cm. These were evaporated to dryness in an oven at 105°C. The supernatant was then decanted and transferred to a 600 ml beaker and the process of addition and decantation of distilled water was repeated until the supernatant was clear. The residue left was the sand fraction. The clay, silt and sand percentage was calculated according to the following equation:

Clay percentage:

$$\frac{W_c \times 100}{W_c + W_s + W_{ts}}$$

Silt percentage:

$$\frac{W_s \times 100}{W_c + W_s + W_{ts}}$$

Sand percentage:

$$\frac{W_{ts} \times 100}{W_c + W_s + W_{ts}}$$

Where W_c = Weight of the oven dried clay fraction.

W_s= Weight of silt in the total volume of 1000 ml suspension.

W_{ts}= Weight of the oven dried sand fraction.

3.1.2 Soil moisture

The soil moisture was expressed on an oven dry weight basis and determined by the overnight drying of samples at 105°C.

3.1.3 Soil organic matter

The soil organic matter was expressed on an oven dry weight basis and determined by the combustion of samples at 800°C for 2 hours.

3.1.4 Soil pH

The soil pH was measured with a pH meter on a suspension of soil in water.

3.2 Extraction of nitrohumic acids (NHAs)

3.2.1 Nitration of coal

Nitrohumic acids were prepared from Mukah coal with the nitration process. The coal sample was ground and sieved through 50 μm sieve prior to the chemical treatment and extraction procedure. The coal sample was pre-treated with 10 % nitric acid prior to extraction. One gram of coal sample was added to 5 ml of nitric acid at 70°C for 2 hours with continuous stirring. The coal was filtered, washed with distilled water and finally oven- dried at 60°C.

3.2.2 Alkali extraction

The extraction method described by the International Humic Substances Society (1983) was adopted with modifications. Ten grams of nitrated coal sample was added to 100 ml of KOH (0.5M) and heated at 70°C for 2 hours. The supernatant was filtered through a 50 μm sieve and the coal residue was washed with distilled water until the wash water was clear. The coal residue was dried at 105°C and weighed. The supernatant was acidified with concentrated H_2SO_4 to pH 1-2 and allowed to stand overnight. The precipitated nitrohumic acids were separated by centrifugation at 6000 rpm for 15 min and the supernatant was discarded. The gel-liked nitrohumic acids were oven-dried at 60°C and stored in desiccators.

3.3 Characterization of nitrohumic acids

The nitrohumic acids samples were subjected to analyses which included moisture content, ash content, total acidity (-COOH plus -OH), functional groups determination, structure determination using FTIR spectroscopy and E_4/E_6 ratio using UV/Vis spectroscopy.

3.3.1 Moisture content

Three replicates of a 0.5 g of nitrohumic acids were weighed and oven-dried overnight at 105°C. The difference in weight was considered as moisture content.

3.3.2 Ash content

The ash content of the nitrohumic acids was obtained after ignition in a muffle furnace at 800°C for 2 hours.

3.3.3 Total acidity (COOH plus phenolics- and/or enolic-OH)

Three replicates of approximately 70 mg of nitrohumic acids were dissolved in 20 ml of 0.2M $Ba(OH)_2$ solution in a 125 ml Erlenmeyer flask. A blank consisting of 20 ml of 0.2 M $Ba(OH)_2$ only was also set up. The air in each flask was displaced by N_2, and shaken for 24 hours at room temperature. The suspension was filtered and the filtrate was titrated with 0.5M HCl solution to pH 8.4. The total acidity (in $meqg^{-1}$) was calculated by the equation:

$$\text{Total acidity} = \frac{(V_b - V_s) \times N}{\text{g of sample}}$$

Where V_b = Volume of standard acid for blank.

V_s = Volume of standard acid for sample.

N = Concentration of the acid.

3.3.4 Carboxyl functional group determination (-COOH)

Three replicates of 70 mg of nitrohumic acids were dissolved in 10 ml of 0.5M $Ca(CH_3COO)_2$ solution and 40 ml of distilled water in a 125 ml Erlenmeyer flask. A blank consisting of 10 ml of 0.5M $Ca(CH_3COO)_2$ solution and 40 ml distilled water only was also prepared. The flasks were then stoppered and shaken for 24 hours at room temperature. The suspension was filtered and the filtrate was titrated with 0.1M NaOH solution to pH 9.8. The content of COOH groups (in $meqg^{-1}$) was calculated by the equation:

$$\text{COOH groups} = \frac{(V_s - V_b) \times N}{\text{g of sample}}$$

Where V_b = Volume of standard base for blank.

V_s = Volume of standard base for sample.

N = Concentration of the base.

3.3.5 Phenolic functional group determination (-OH)

Phenolic content was calculated as the difference between total acidity and carboxyl groups.

3.3.6 Structure determination using Infrared Spectroscopy (FTIR)

The functional groups present in the nitrohumic acids were characterized by Fourier-Transform Infrared (FTIR) spectroscopy. KBr disc consisting of 2 mg of nitrohumic acid sample and 100 mg KBr was prepared for analysis.

3.3.7 E_4/E_6 ratio determination using UV/Vis Spectroscopy

Five milligrams of nitrohumic acids were dissolved in 25 ml of 0.05 M $NaHCO_3$ solution. The absorbance of the mixture at 465 and 665 nm were recorded on the *Perkin Elmer Lambda 11 UV/VIS* spectrometer. The ratio of absorbance at 465 and 665 nm is referred to as E_4/E_6.

3.4 Aggregate Stability Measurements

3.4.1 Preparation of nitrohumate stock solutions

Five nitrohumate stock solutions were prepared separately by dissolving 0.005 g, 0.01 g, 0.05 g, 0.10 g and 1.0 g of nitrohumic acids in 30 ml of distilled water. 0.1 M NaOH were added drop wise until the pH stabilized at 7.0. The final volumes were then made up to 50 ml. A control of distilled water was also prepared simultaneously.

3.4.2 Aggregate stability experiments

Dry aggregates of 2-5 mm were separated by dry sieving for aggregate stability experiments. The nitrohumate solutions were mixed with 100 g of 2-5 mm air-dry aggregates (considered to be most stable to wetting; Lanyon, 2001) to yield the following treatment rates: 0.0, 0.05, 0.10, 0.50, 1.0 and 10 g/kg. These soil samples amended with nitrohumic acids were homogenized and incubated for 15 days at 25 ^{o}C prior to aggregate stability study.

3.4.3 Determination of aggregate stability

Aggregate stability of the soil samples was measured by the wetting and drying procedure. According to Imbufe *et al.* (2005), wetting and drying conditions contribute to reduction of aggregate stability. The soil aggregates break down into smaller aggregates as a consequence of fractures produced during the shrinkage and swelling process. These micro-aggregates are more susceptible to erosion and dispersion. The incubated soil samples were air-dried and sieved to obtain 2-1 mm aggregates. Three grams of the 2-1 mm aggregates were weighted and distributed in a 0.5 mm mesh sieve and placed into a 10 L beaker and the water level raised 20 mm above the base of the screen. The aggregates were allowed to sit overnight and

manually agitated 20 times on the following day (Note: Do not raise the sieve so high to avoid air bubbles). The 0.5 mm sieve containing the particles was removed and oven dried at 105°C for 2 hours. The aggregate stability (%) was calculated according to the following equation:

$$\text{Aggregates (\%)} = \frac{W_R - S_W}{3.00 - S_W} \times 100$$

Where W_R = Total weight of aggregates retained on 0.5 mm sieve.

S_W= Weight of 2.0 to 0.5 mm sand.

The aggregate stability calculated upon completion of the above described procedure is referred to as one cycle. The procedure was repeated for 2, 3, 4 and 5 cycles on the same sample.

3.5 Statistical Analysis

Analysis of variance (ANOVA) was employed to investigate the significant difference between the aggregate stability and the application rates.

4. RESULTS AND DISCUSSION

4.1 The soil analyses

Table 1: Characteristics of soil samples

Properties	TUDM A
Texture	Loamy sand
Sand, %	83.57
Silt, %	0
Clay, %	16.43
Aggregate stability (1 cycle), %	43
Soil moisture, %	0.5 ± 0.04
Organic matter, %	0.38 ± 0.05
Erosion Index, (sand+silt/ OM+clay)	4.97
pH	4.59

Table 1 shows the characteristics of the soil sample. The soil sample was classified as loamy sand based on the soil texture triangle (refer to Figure 2), consisting of a major portion of sand particles. The attraction of the sand particles is poor therefore the nutrient holding capability of loamy sand is low (Brady and Weil, 1996). For this reason, the loamy sand is susceptible to erosion, affecting the suitability of the soil for plant growth. Erosion can be measured using erosion index, El. Lower El value indicates better soil stability (Piccolo *et al.*, 1997). It is affected by soil properties such as organic matter content, soil texture, swelling clays content and soil depth (Brady and Weil, 1996).

The organic matter content of the loamy sand sample was low, indicating poor aggregate stability. Chaney and Swift (1984) revealed a highly significant linear correlation between the aggregate stability and the organic matter content. The organic matter is important for binding of the mineral particles onto the soil granular thus stabilizing the soil structure (Brady and Weil, 1996). They also found correlation between soil aggregate stability, moisture content